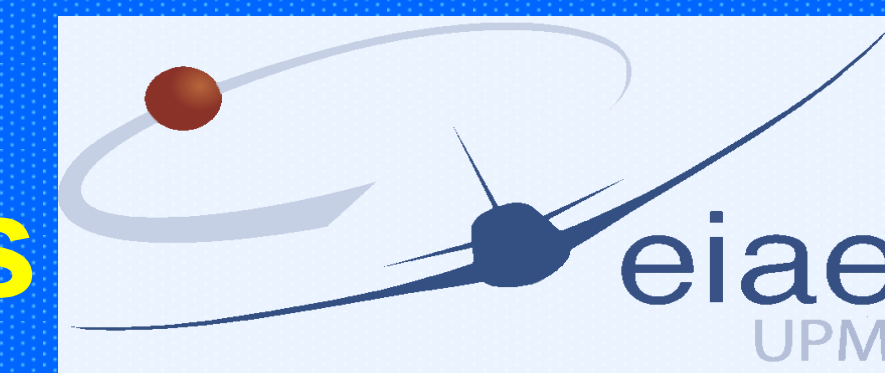




# Influence of the epoxy/amine stoichiometry on the thermomechanical properties of nanocomposites based on high $T_g$ epoxy and organophilic clays



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Escuela de Ingeniería  
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## INTRODUCTION

In layered silicate-epoxy nanocomposites organic modification of the silicates makes them compatible with the epoxy which intercalates into the clay galleries. The effect of clay dispersion on epoxies of high  $T_g$  is not clear. Decreases of the epoxy  $T_g$  have been frequently reported. The presence of clay may cause stoichiometry imbalances that conduces to the formation of imperfect networks.

## EXPERIMENTAL

**Dispersion:** Clay was dispersed in DGEBA at 120°C Vacuum 80°C. Addition of DDM 2min. Sonication.

### Curing protocols

- I dynamic curing in the DSC at 10°C/min
- II curing in oven: 2h-120°C + 1h- 180°C

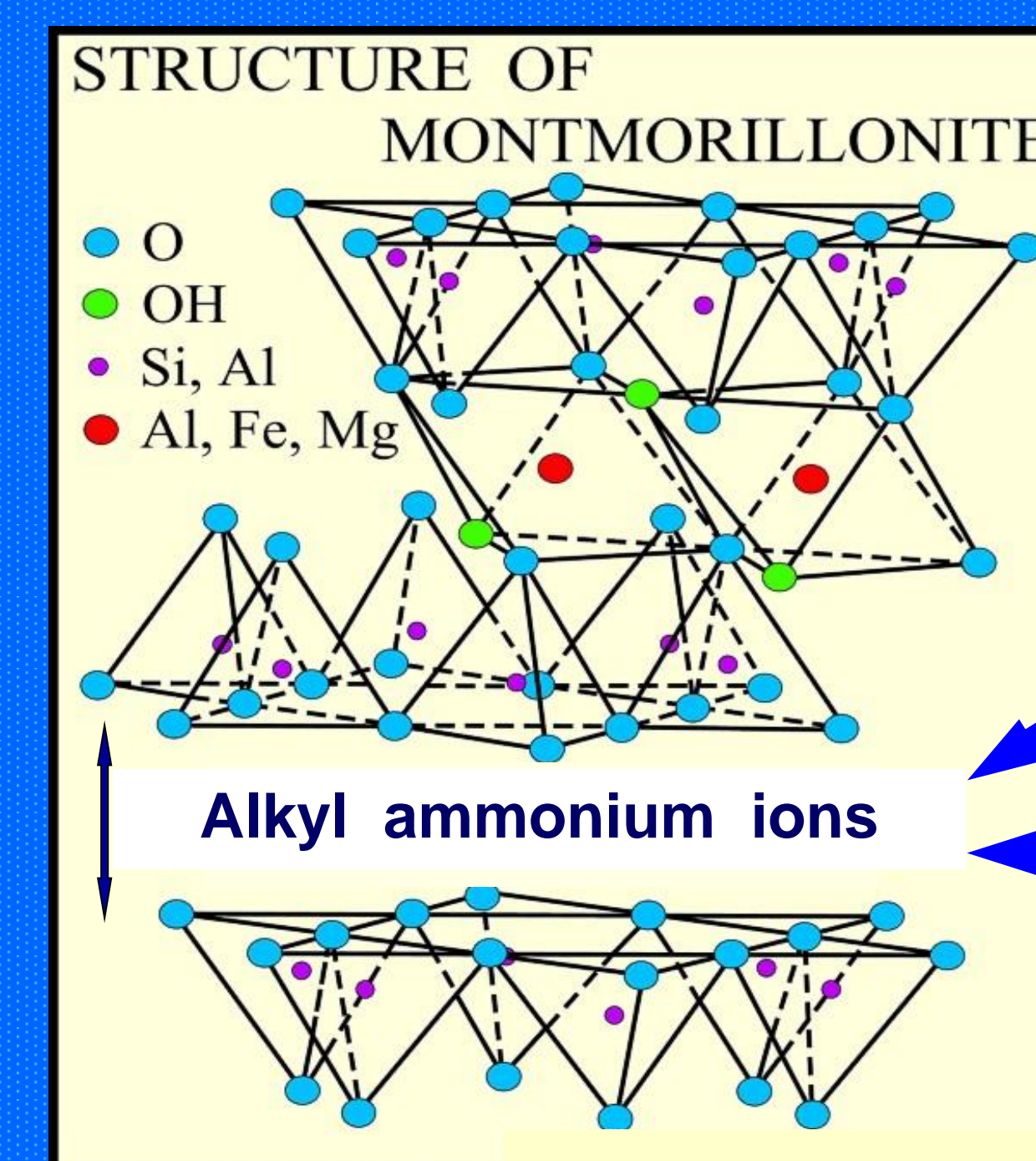
### Materials

- **Cloisites:** C30B and C93A
- Diglycidyl ether of bisphenol A, **DGEBA**
- 4,4'-diaminodiphenylmethane, **DDM**
- **Stoichiometric ratio:**  $r = \text{HN/O-} = 0.85$  to 1.15

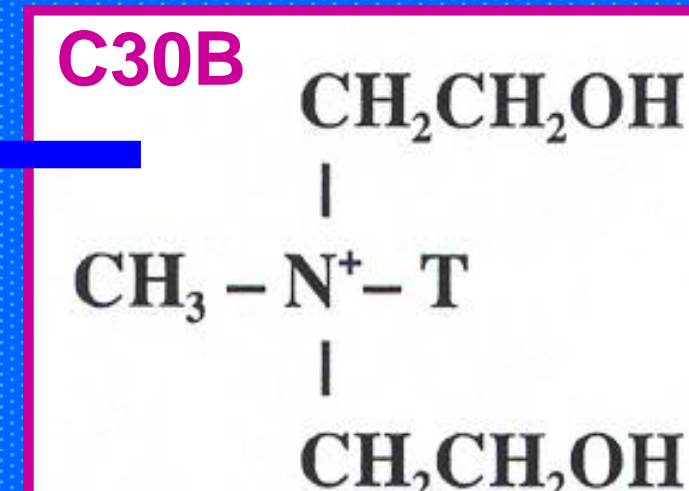
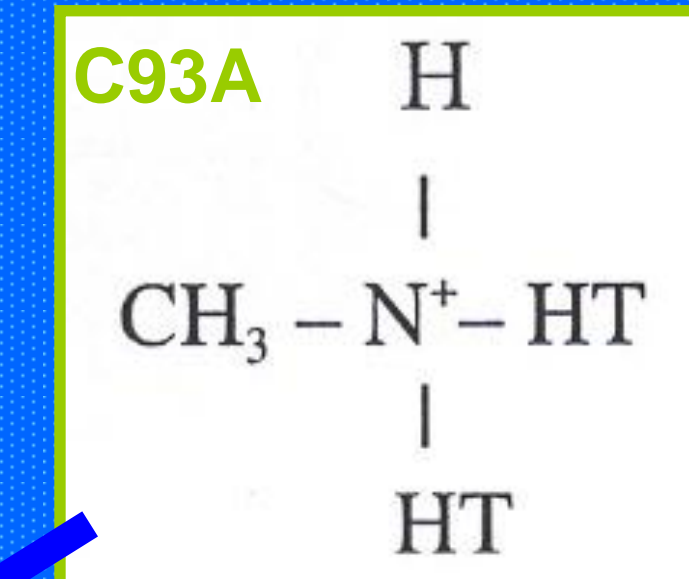
## RESULTS AND DISCUSSION

## OBJECTIVE

To study off-stoichiometry effects in clay-epoxy nanocomposites by analyzing: its influence on curing, glass transition temperature, thermomechanical and mechanical properties of the nanocomposites.

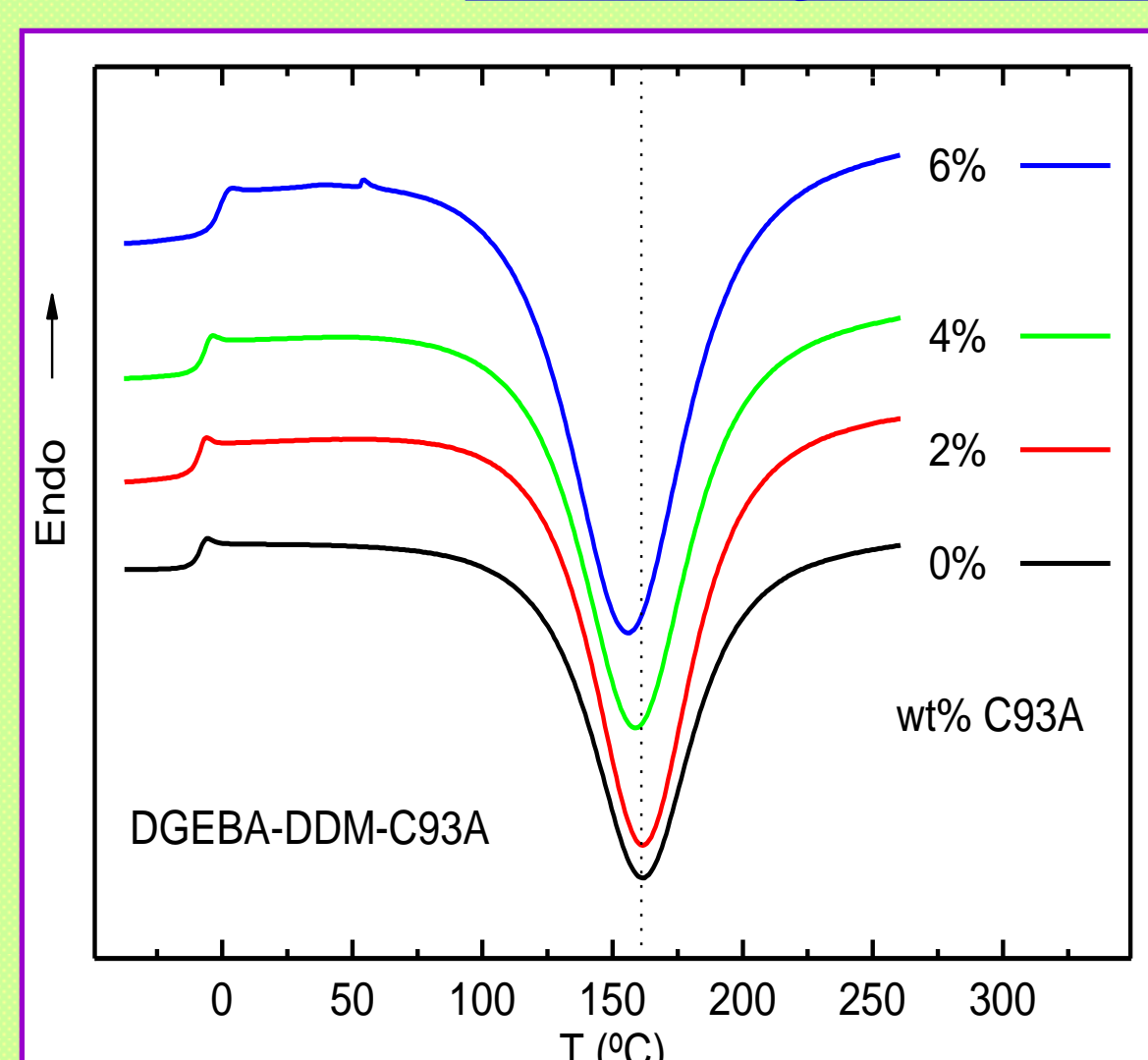


### CLOISITES

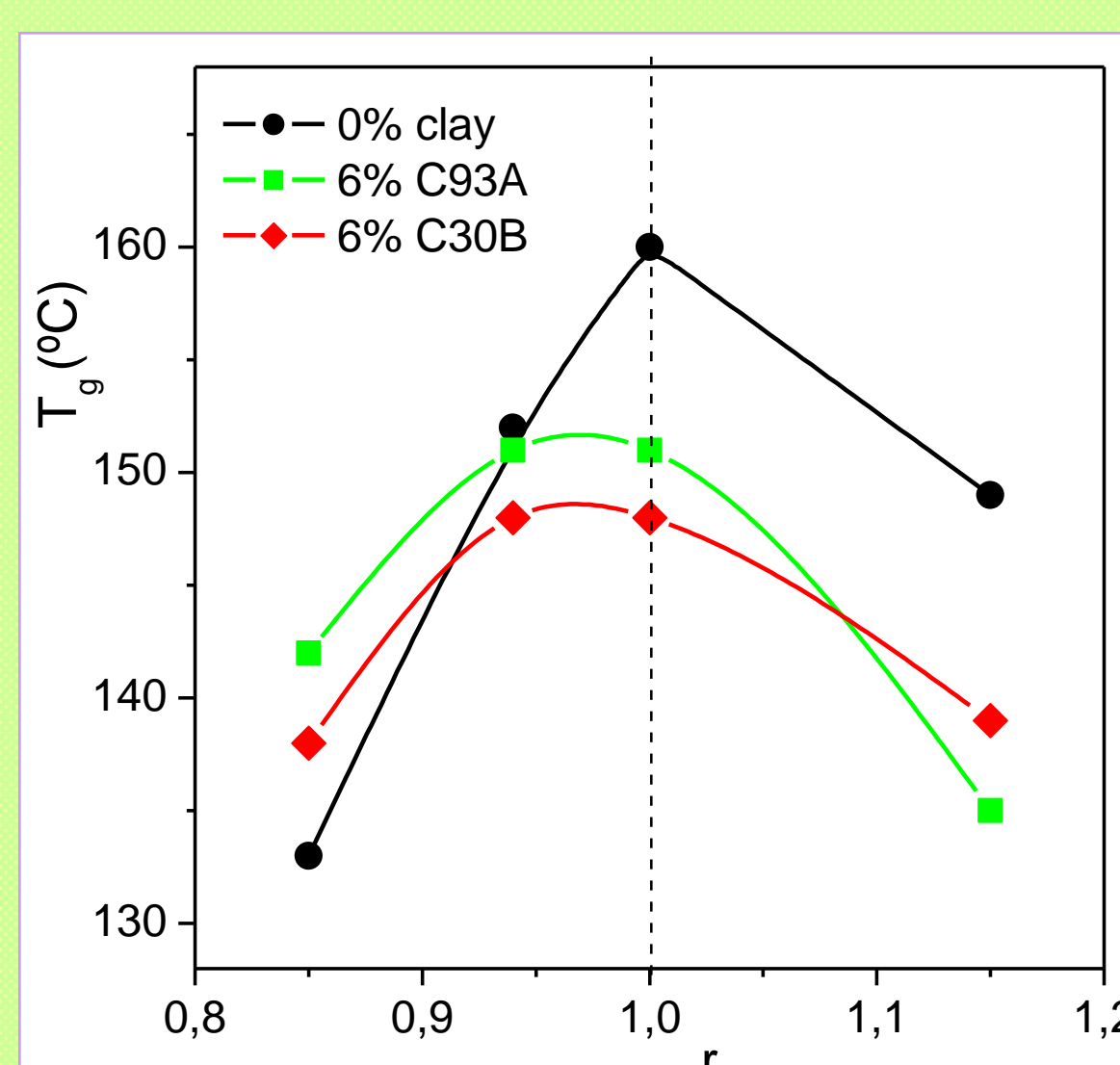
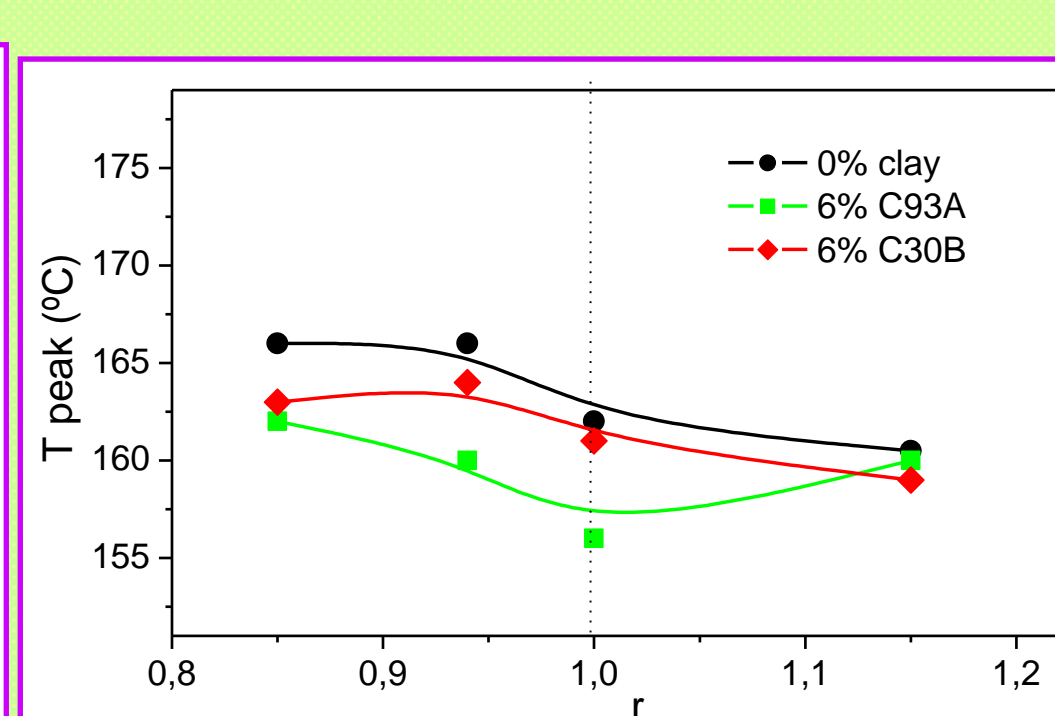
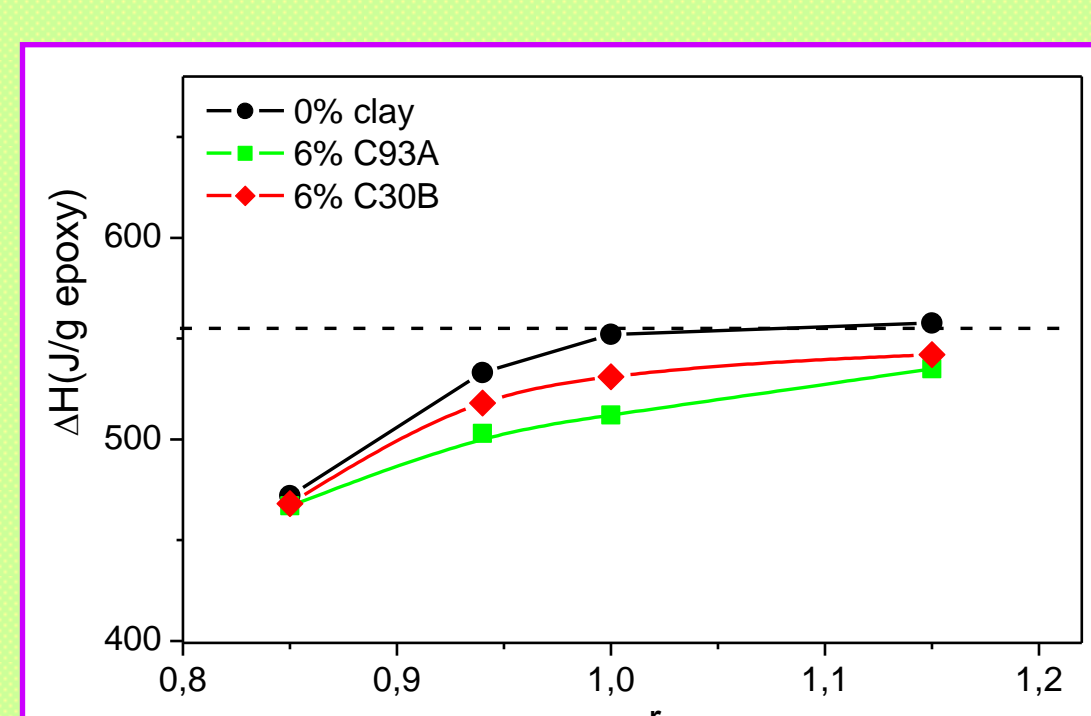


T $\equiv$  tallow, HT $\equiv$  hydrogenated tallow: 65% C18, 30%C16, 5%C14

### DSC: Dynamic curing of clay-epoxy dispersions



**C93A-DGEBA-DDM and C30B-DGEBA-DDM** the exothermal peak temperature shifts to lower values  $\rightarrow$  the clays accelerate the curing reaction

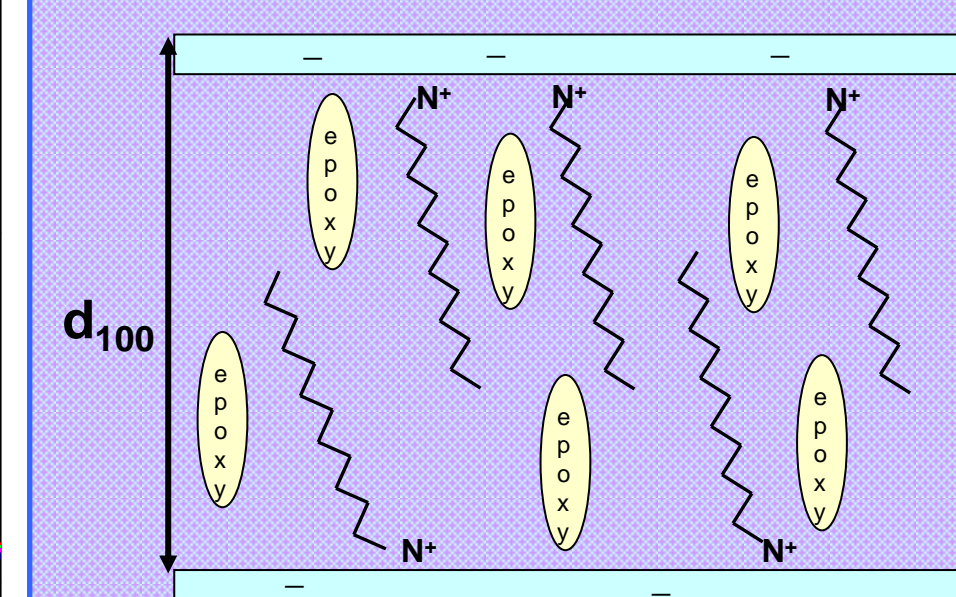
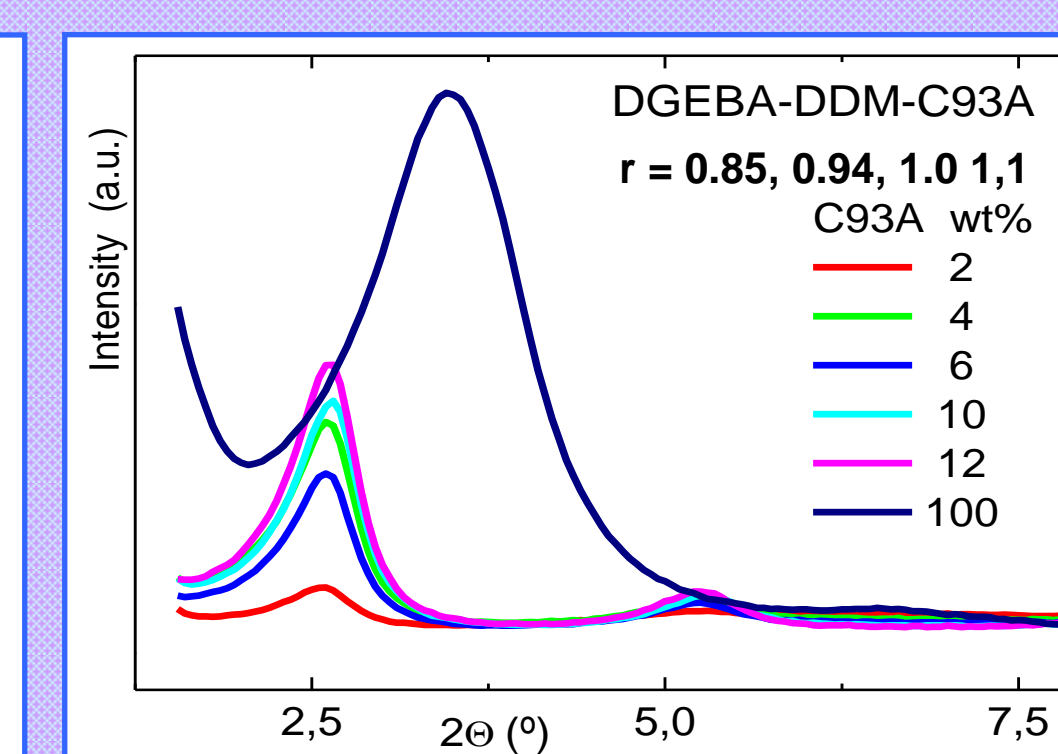
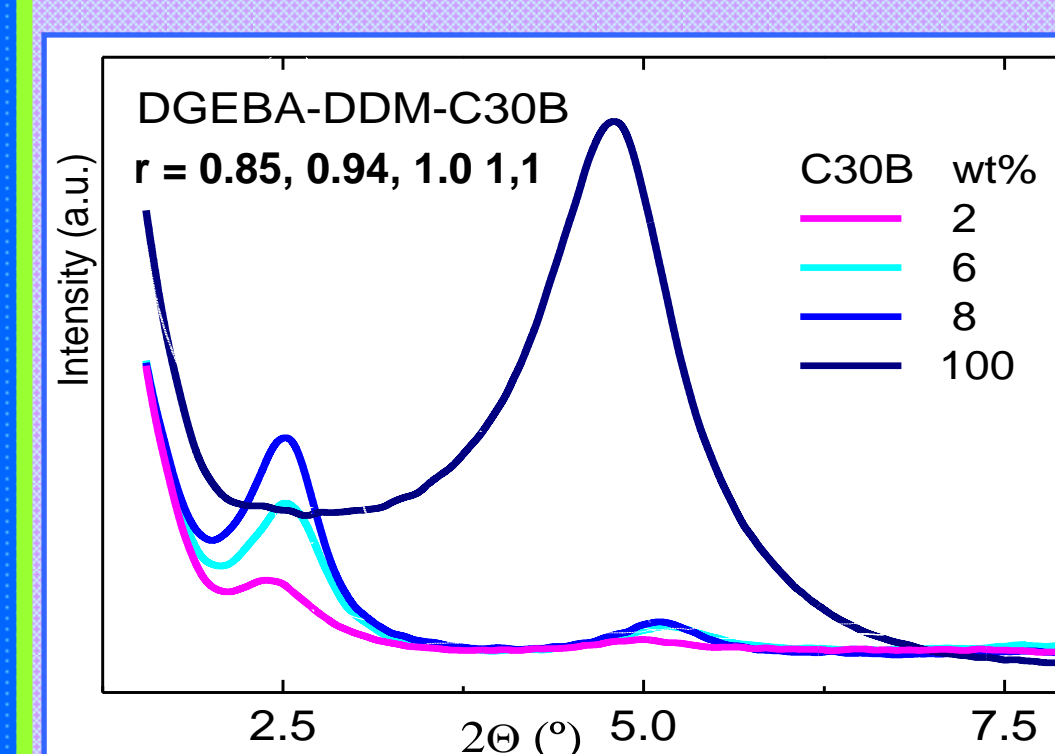


$\Delta H$  (J/g epoxy) is lower in nanocomposites than in neat epoxy for  $r > 0.85$ . The lowest values of  $\Delta H$  (J/g epoxy) were observed in C93A nanocomposites.

The curing reaction slows when  $r$  increases

- Neat epoxy thermosets:  $T_g$  maximum appears at  $r = 1$
- Nanocomposites: the maximum of  $T_g$  occurs at  $r < 1$
- For  $r > 0.94$  the presence of clays lowers  $T_g$
- For  $r \approx 0.85$  the presence of clays raises  $T_g$

### WAX-ray Diffraction of nanocomposites

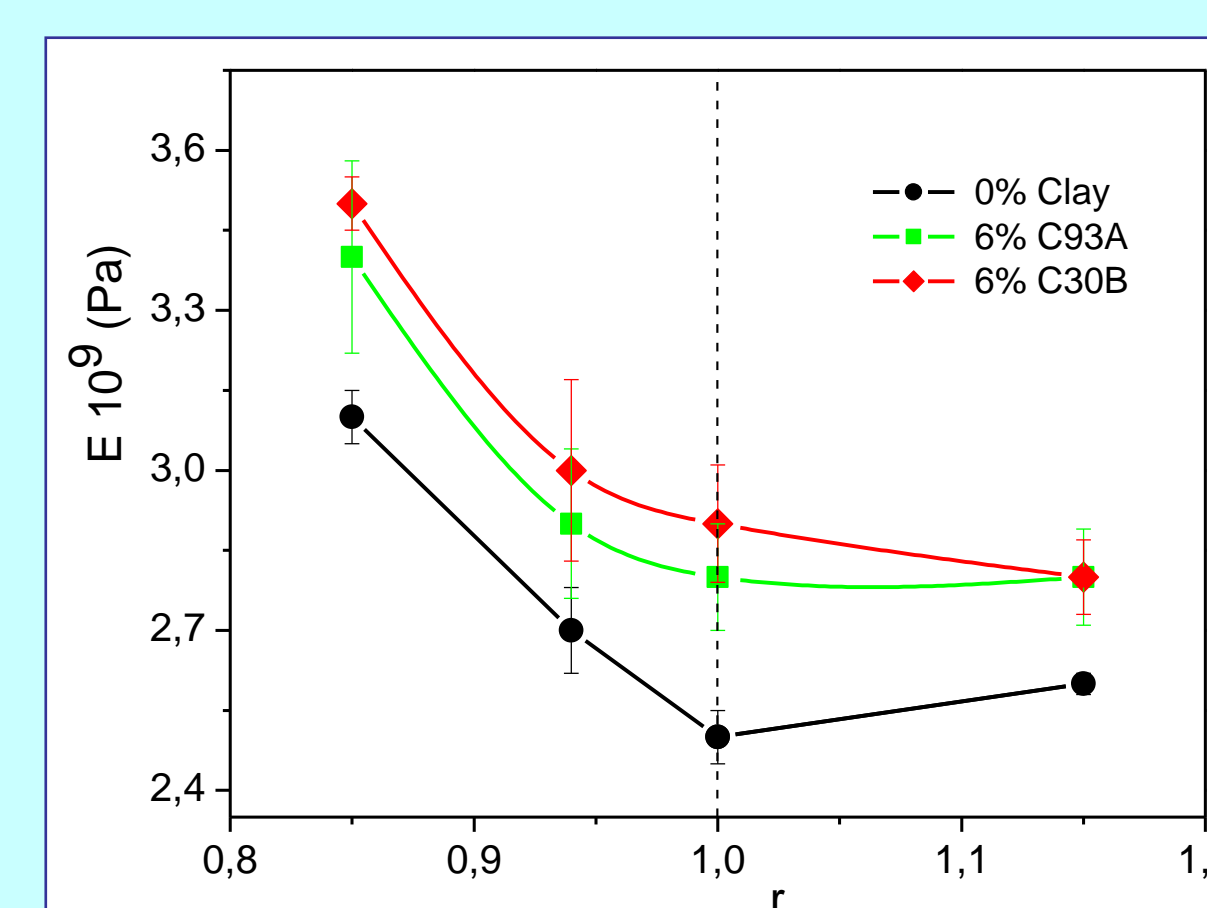


Basal distance  $d_{001}$  (nm)

Clay	neat clay	clay-epoxy nanocomposite
C30B	1.82	3.4
C93A	2.56	3.3

**Nanocomposites show intercalated structures**  
 $\Delta d_{001} \text{ C30B} > \Delta d_{001} \text{ C93A}$

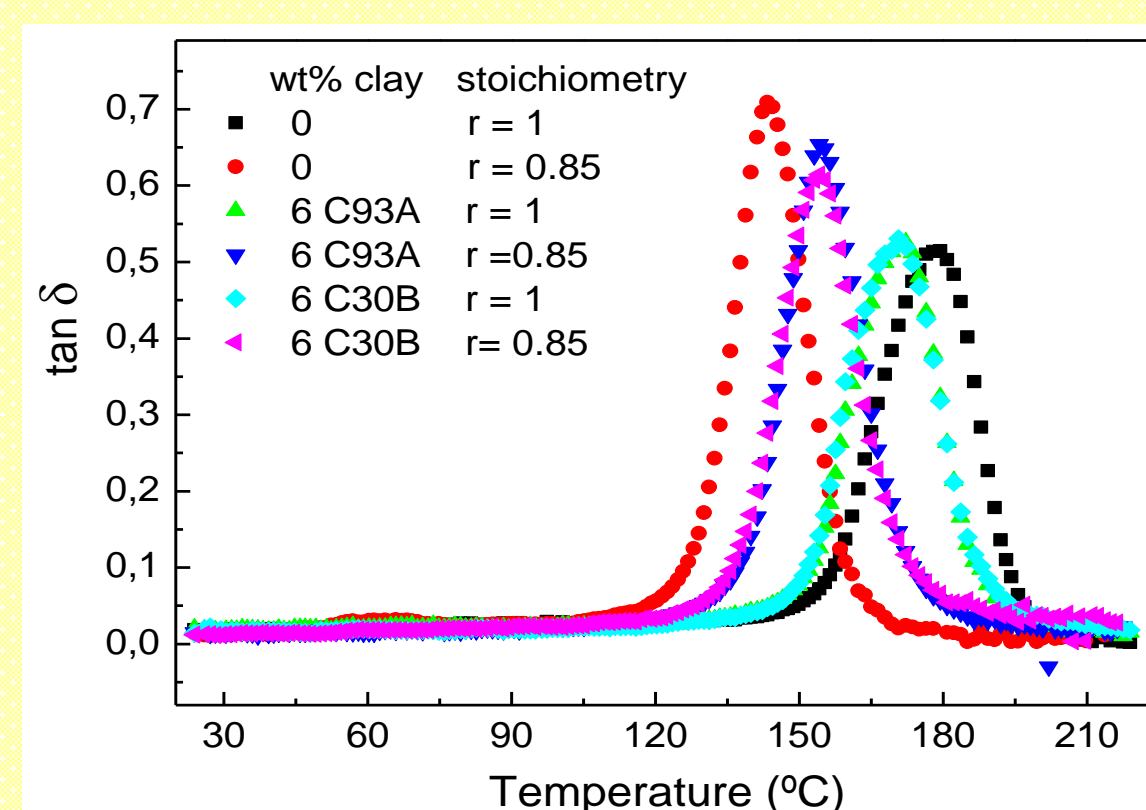
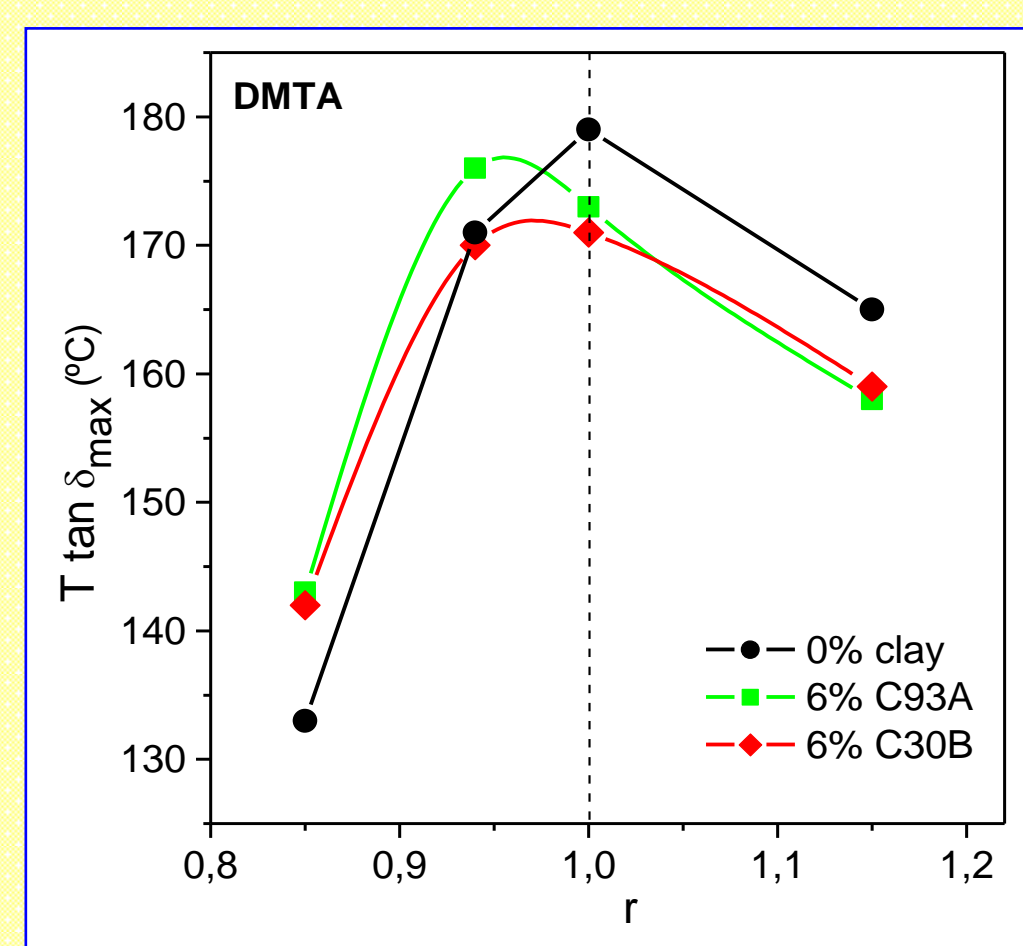
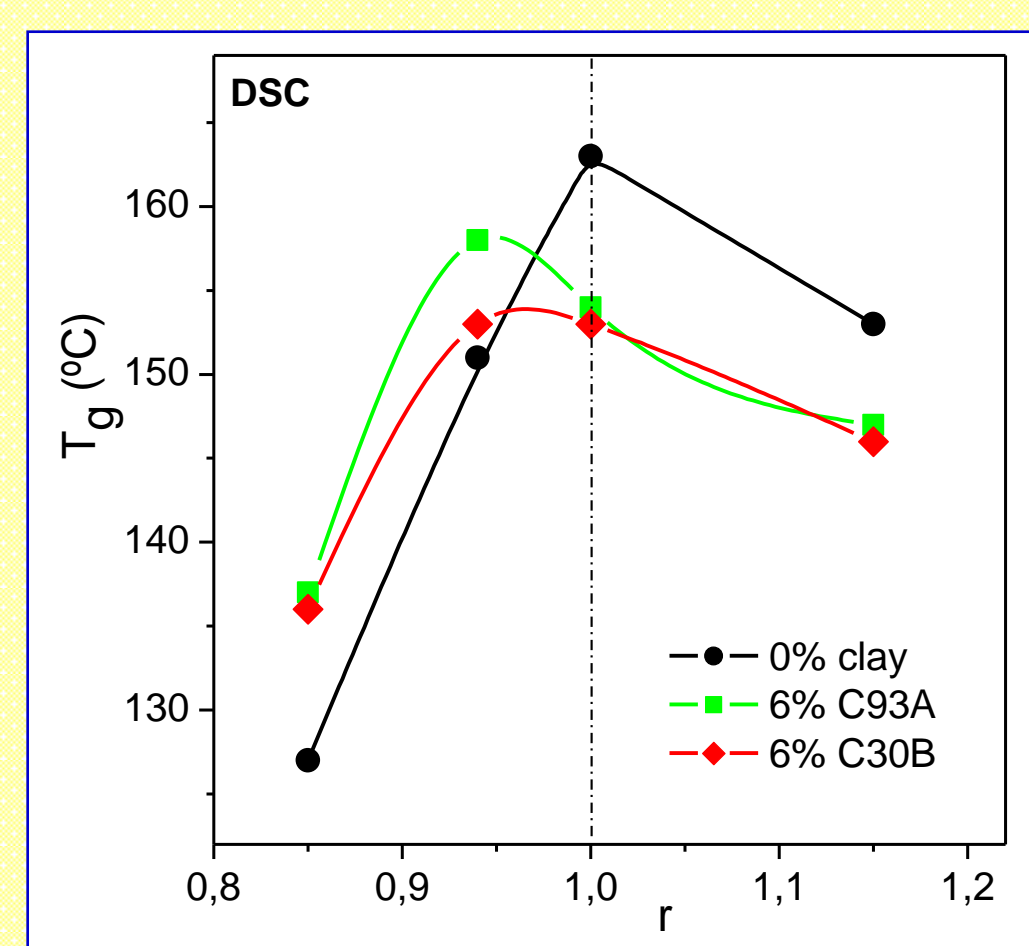
### Nanocomposites cured under protocol II: Tensile tests at 25°C



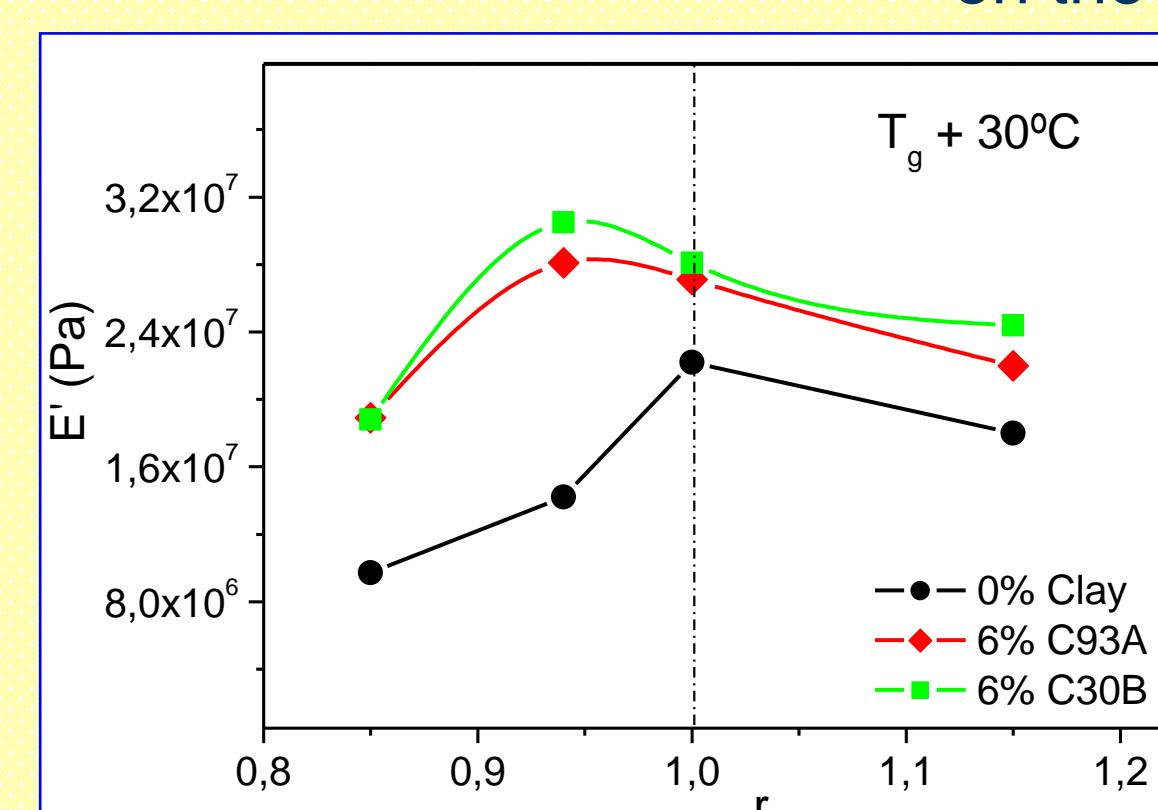
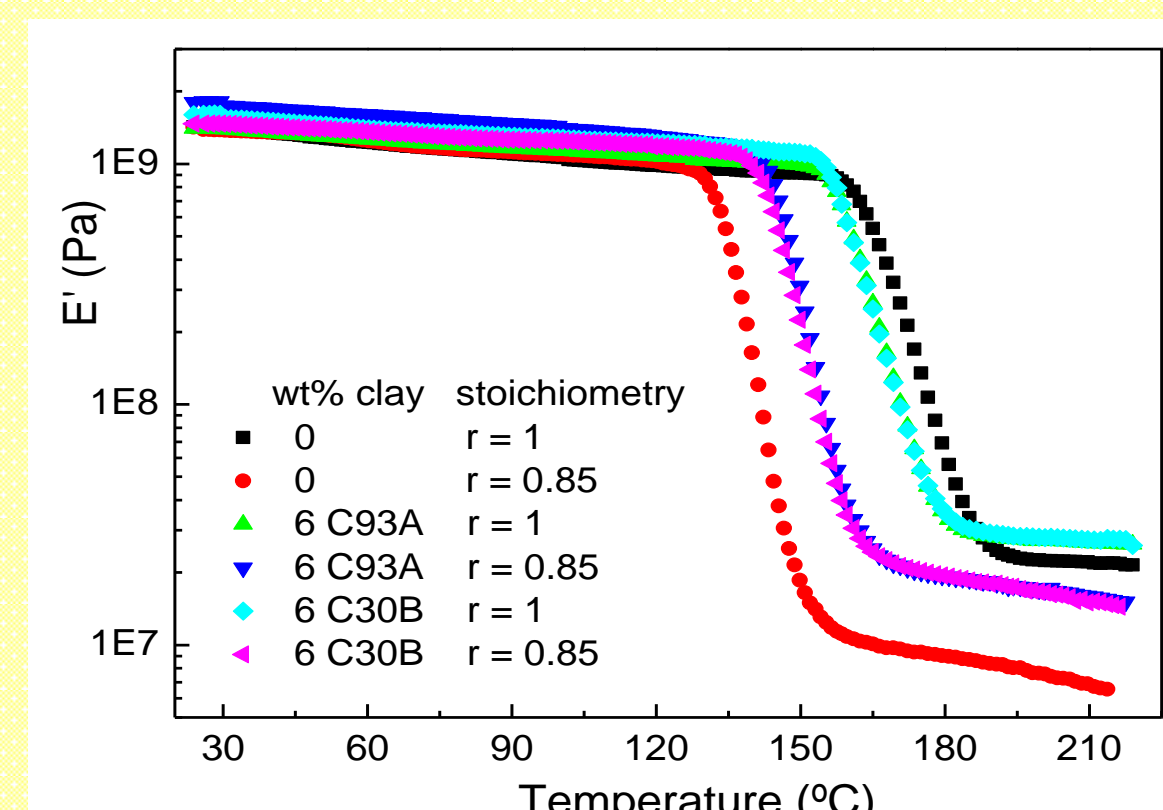
**Glassy state:** the highest modulus is observed in epoxy-rich compositions ( $r < 1$ ).

A minimum in the modulus appears at  $r = 1$  for neat epoxy thermoset, this behaviour has been explained in base of network topology and packing density.

### Nanocomposites cured under protocol II: DSC & DMTA



The  $T_g$ - $r$  trend is almost independent on the curing protocol



$E'_{\text{rubber}}$  and  $T_g$  show similar behaviour: maximum values in  $T_g$  and in  $E'_{\text{rubber}}$  are coincident  $\rightarrow$  highest crosslinking density

**Rubber state:** clay-epoxy nanocomposites have higher  $E'_{\text{rubber}}$  than neat epoxy thermosets for  $r \leq 0.94$ , but lower for  $r > 1$ .

## CONCLUSIONS

- **Stoichiometry** is an important factor determining epoxy thermoset properties, both in epoxy neat thermosets and clay-epoxy nanocomposites.
- **Similar property-stoichiometry trends** are observed in epoxy neat thermosets and clay-epoxy nanocomposites, but the behaviour of nanocomposites is shifted toward lower stoichiometric ratios.
- The presence of clays modify the stoichiometry, curing and properties.